



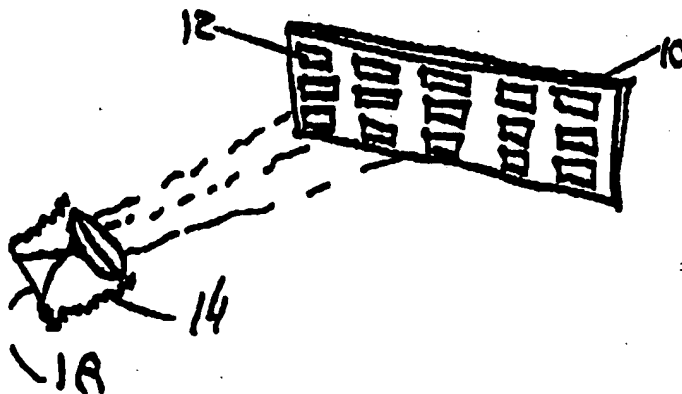
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification <sup>6</sup> :<br><b>G01N 31/10</b>   | <b>A1</b>  | (11) International Publication Number: <b>WO 97/32208</b><br>(43) International Publication Date: <b>4 September 1997 (04.09.97)</b> |
| <p>(21) International Application Number: <b>PCT/US97/02756</b></p> <p>(22) International Filing Date: <b>25 February 1997 (25.02.97)</b></p> <p>(30) Priority Data:<br/>60/012,457      28 February 1996 (28.02.96)      US<br/>08/664,836      17 June 1996 (17.06.96)      US</p> <p>(71) Applicant (for all designated States except US): <b>TECHNOLOGY LICENSING CO. L.L.C. [US/US]; 4th floor, 1401 Winchester Avenue, Ashland, KY 41101 (US).</b></p> <p>(72) Inventor; and<br/>(75) Inventor/Applicant (for US only): <b>WILLSON, Richard, Coale, III [US/US]; 5147 Birdwood Drive, Houston, TX 77096 (US).</b></p> <p>(74) Agent: <b>WILLSON, Richard, Coale, Jr.; 4th floor, 1401 Winchester Avenue, Ashland, KY 41101 (US).</b></p> | <p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TO).</b></p> <p><b>Published</b><br/><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> |  |

(54) Title: **CATALYST TESTING PROCESS AND APPARATUS**

## (57) Abstract

A multicell holder (10) e.g. a honeycomb or plate, or a collection of individual support particles, is treated with solutions/suspensions of catalyst ingredients to produce a plurality of cells, spots, or pellets (12) each having a different composition. The plurality of cells, spots, or pellets are dried, calcined or treated to stabilize the ingredients and contacted with a potentially reactive feed stream or batch of reactants. The reaction occurring in each cell (12) is measured or analyzed to determine the relative efficacy of the catalysts in each combination. The measurement or analysis is done through a number of different methods including infrared thermography (14), spectroscopy of products or residual reactants or sampling for further analysis. Robotic techniques can be employed in producing the cells, spots or pellets (12).



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| (54) Title: <b>MASS SPECTROMETERS AND METHODS FOR RAPID SCREENING OF LIBRARIES OF DIFFERENT MATERIALS</b>   |  |   |  |
| (57) Abstract   |  |   |  |
| <p>Methods and apparatus for screening diverse arrays of materials are provided. In particular, techniques are provided for rapidly characterizing compounds in combinatorial arrays of materials for discovering and/or optimizing new materials with specific desired properties. According to one aspect, a scanning mass spectrometer is used which includes an ionization chamber and a collector that outputs an electrical signal responsive to the quantity of gas ions contacting the collector surface. A conduit system selectively withdraws samples from the array of materials, passing the samples into the ionization chamber. In a specific embodiment, reactants are passed through the conduit system to the selected regions of interest on the substrate. Means are provided to selectively heat regions on the substrate.</p> |  |   |  |
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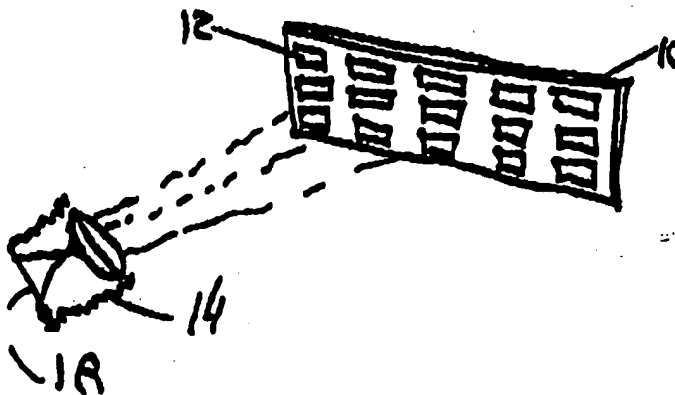
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A multicell holder (10) e.g. a honeycomb or plate, or a collection of individual support particles, is treated with solutions/suspensions of catalyst ingredients to produce a plurality of cells, spots, or pellets (12) each having a different composition. The plurality of cells, spots, or pellets are dried, calcined or treated to stabilize the ingredients and contacted with a potentially reactive feed stream or batch of reactants. The reaction occurring in each cell (12) is measured or analyzed to determine the relative efficacy of the catalysts in each combination. The measurement analysis is done through a number of different methods including infrared thermography (14), spectroscopy of products or residual reactants or sampling for further analysis. Robotic techniques can be employed in producing the cells, spots or pellets (12).



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# Catalyst Testing Process and Apparatus

## Background of the Invention

### I. Field of the Invention:

The present invention relates to the general field of catalyst testing, negerally classified in U.S. Patent Class 502 or 252. The present invention relates to the general field of catalyst testing, generally classified in U. S.

10 Patent Class 502 or 252.

### II. Description of the Prior Art

Prior Art will include C & E News, 8 Jan. 96, p.30 which teaches reactive plastics, and the many catalyst testing devices and processes known to the petroleum refining art.

- 15 F.M. Menger, A.V. Eliseev, and V.A. Migulin, "Phosphatase catalysts developed via combinatorial organic chemistry", J. Org. Chem. Vol. 60, pp 6666-6667, 1995. Xiang, 268 Science 1738 and Briceno, 270 Science 273, both on combinatorial libraries of solid-state compounds; Sullivan, Today's Chem.
- 20 At Work 14 on combinatorial technology; Nessler 59 J. Org. Chem. 4723 on tagging of combinatorial libraries; Baldwin, 117 J. Amer. Chem. Soc. 5588 on combinatorial libraries.

### II. Problems Presented by Prior Art

25

Catalyst testing is conventionally accomplished in bench scale or larger pilot plants in which the feed is contacted with a catalyst under reaction conditions, generally with effluent products being sampled, often with

samples being analyzed and results subjected to data resolution techniques. Such procedures can take a day or more for a single run on a single catalyst. While such  
5 techniques will have value in fine-tuning the optimum matrices, pellet shape, etc., the present invention permits the scanning of dozens of catalysts in a single set-up, often in less time than required for a single catalyst to be evaluated by conventional methods. Further, when practiced  
10 in its preferred robotic embodiments, the invention can sharply reduce the labor costs per catalyst screened.

## Summary of the Invention

### General Statement of the Invention

According to the invention, a multisample holder  
15 (support) e.g., a honeycomb or plate, or a collection of individual support particles, is treated with solutions/suspensions of catalyst ingredients to fill wells in plates, or to produce cells, spots or pellets, holding each of a variety of combinations of the ingredients, is  
20 dried, calcined or otherwise treated as necessary to stabilize the ingredients in the cells, spots or pellets, then is contacted with a potentially reactive feedstream or batch e.g., to catalyze biochemical reactions catalyzed by proteins, cells, enzymes; gas oil, hydrogen plus oxygen,  
25 ethylene or other polymerizable monomer, propylene plus oxygen, or  $\text{CCl}_2\text{F}_2$  and hydrogen. The reaction occurring in each cell is measured, e.g. by infrared thermography, spectroscopic, electrochemical, photometric, thermal conductivity or other method of detection of products or

residual reactants, or by sampling, e.g. by multistreaming through low volume tubing, from the vicinity of each combination, followed by analysis e.g. spectral analysis, chromatography tc, or by observing temperature change in the vicinity of the catalyst e.g. by thermographic techniques, to determine the relative efficacy of the catalysts in each combination. Robotic techniques can be employed in producing the cells, spots, pellets, etc..

10 Each of these parameters is discussed below:

Catalysts: Biotechnology catalysts include proteins, cells, enzymes, etc. Chemical conversion catalysts include most of the elements of the periodic table which are solid at the reaction conditions. Hydrocarbon conversion catalysts include Bi, Sn, Sb, Ti, Zr, Pt, the rare earths, and many possible candidates whose potential has not yet been recognized for the specific reaction. Many synergistic combinations will be useful. Supported metals and metal complexes are preferred. The chemical catalysts can be added to the substrate (support) as elements, as organic or inorganic compounds which decompose under the temperature of the stabilizing step, depositing the element or its oxide onto the substrate, or as stable compounds.

Supports: Supports can be inert clays, zeolites, ceramics, carbon, plastics, e.g. reactive plastics, stable, nonreactive metals, or combinations of the foregoing. Their shape can be porous honeycomb penetrated by channels, particles (pellets), or plates onto which patches (spots) of catalyst candidates are deposited or wells in plates.

30 Conventional catalyst matrix materials such as zeolites' e.g.

z olite USY, kaolin, alumina, etc. are particularly preferred as they can simulate commercial catalysts.

Preparation: The catalyst candidate precursors can be

- 5 deposited onto the supports by any convenient technique, preferably by pipette or absorbing stamp (like a rubber stamp), or silk screen. In preferred embodiments, the deposition process will be under robotic control, similar to that used to load multicell plates in biochemical assays.
- 10 Many of the spots of catalyst will be built up by several separate depositions e.g. a channel penetrating a honeycomb can be plugged at one third of its length and the channel filled with a catalyst solution in its upper third, then the plug can be moved to the two-thirds point in the channel and
- 15 a second catalyst pipetted in, then the plug can be removed and a third catalyst solution added, resulting in a channel in which reactants contact three catalysts successively as they flow through the channel. Catalyst can also be added by ion exchange, solid deposition, impregnation, or
- 20 combination of these. The techniques of combinatorial chemical or biological preparation can preferably be utilized to prepare an array of candidate catalysts with the invention. Coprecipitates of two or more catalysts can be slurried, applied to the support, then activated as
- 25 necessary. Catalysts can be silk screened onto a support plate or inside of a support conduit, and successive screenings can be used to add different catalyst combinations to different spots.

Stabilizing Step: Once the catalysts are in place on the

30 support, any suitable technique known to the art can be used to stabilize, and/or activate the particular catalysts



chosen, so they will remain in place during the reaction step. Calcining, steaming, melting, drying, precipitation and reaction in place will be particularly preferred.

- 5 Reactants: The invention has utility with any reaction which can be enhanced by the presence of a catalyst, including biological reactions and inorganic and organic chemical reactions. Chemical reactions include polymerization reactions, halogenation, oxidation, hydrolysis,
- 10 esterification, reduction and any other conventional reaction which can benefit from a catalyst. Hydrocarbon conversion reactions, as used in petroleum refining are an important use of the inventions and include reforming, fluid catalytic cracking, hydrogenation, hydrocracking,
- 15 hydrotreating, hydrodesulfurizing, alkylation and gasoline sweetening .

- Sensors: The sensors used to detect catalytic activity in the candidate catalysts are not narrowly critical but will preferably be as simple as practical. Chromatographs,
- 20 temperature sensors, and spectrometers will be particularly preferred, especially those adapted to measure temperature and/or products near each specific catalyst spot e.g. by multistreaming, multitasking, sampling, fiber optics, or laser techniques. Thermography, as by an infrared camera
- 25 recording the temperature at a number of catalyst sites simultaneously, is particularly preferred. Other suitable sensors include electrochemical, fluorescence detectors, NMR, NIR, FTNIR, Raman, flame ionization, thermal conductivity, mass, viscosity and stimulated electron or
- 30 X-ray emission Sensors can detect products in a gas or liquid stream or on the surface of the support. Endothermic

reactions exhibit reduced temperature at best catalysts.

Some sensors employ an added detection reagent, e.g. ozone to impart chemiluminesce.

- 5 Taggants: Optionally taggants (labels) can be added to identify particular catalysts, particularly where particles are employed as the supports for the catalysts. These taggants can be conventional as discussed in the literature. Taggants can be chemicals which are stable at reaction
- 10 conditions or can be radioactive with distinctive emissions. The techniques of combinatorial chemistry will be applicable with taggants as well as with catalysts chosen to suit the particular reaction to be enhanced by the catalyst.
- Batch or Continuous: While the invention will be preferred
- 15 on a flow basis, with reactants flowing by the catalyst spots under reaction conditions, batch testing e.g. in a stirred autoclave or agitated containers, can be employed, particularly in biological reactions.

- Temperatures, pressures, space velocities and other reaction
- 20 conditions: These will be determined by the reactants and reaction. Elevated pressures can be provided as reaction conditions by encasing the support in a reaction chamber with a sapphire or similar window for observation by the sensing means, or with pressure-tight leads extending
- 25 through the reactor walls.

## II. Utility of the Invention

- The present invention is useful in the testing of catalysts for biotechnology, for promotion of gas phase and liquid phase reactions; under batch or, preferably, continuous
- 30 flowstream conditions; at elevated, reduced or atmospheric

pressure; and saves both elapsed time and labor in screening for improved catalysts to promote a desired reaction.

### Brief Description of the Drawings

5           Figure 1 is a schematic diagram of a preferred honeycomb support with a robotic pipetting device depositing different combinations of catalyst ingredients into each of the channels running through the honeycomb, which is thereafter calcined to stabilize the catalysts in each  
10 channel.

Figure 2 is shows schematically the honeycomb of Fig. 1 being contacted by reactants flowing through the channels.

Figures 3a and 3b are alternative schematic diagrams of one channel of the honeycomb of Fig. 2 with a detector  
15 sensing the products exiting the channel by measuring absorption in a laser beam directed through the products or the channel.

Figure 4a shows a channel plugged at its midpoint prior to receiving a solution of catalyst and Figure 4b shows the  
20 plug moved to the end of the channel, so as to form a channel having one catalyst in one half its length and another catalyst in its other half.

Figure 5 shows schematically a sheet of support onto which 15 spots of different catalyst combinations have been  
25 deposited, as discussed in example 1.

Figure 6a shows an array of particles (pellets) of support in place in a reactor after having been ion  
exchanged with different catalyst combinations on different pellets (denoted schematically by different markings on the  
30 pellets in the Figure). Figure 6b shows a packed reactor which is less preferred because upstream pellets see fresh

feed, while downstream pellets see partially reacted feed.

## Description of the Preferred Embodiments

### **Example 1.**

5 Referring to Figure 1, a sheet of alpha alumina 10 is wash coated with particles of porous gamma-alumina by standard methods. Solutions of oxalate salts of 12 different transition metal elements are prepared in the wells of a 24 well microtiter dish made of polystyrene. A  
10 Beckman Biomek 2000 robotic automated liquid handling system is used to prepare dilutions and mixtures from the original stocks, again in the wells of microtiter style plates. The robot is used to deposit 20 microliter aliquots of each of the resulting solutions at defined positions (spots) 12 on  
15 the surface of the alumina support 10, which is then dried, calcined and inserted into a reactor capable of temperature control at temperatures from 100 to 350 degrees centigrade. After reduction, a potentially reactive mixture of oxygen and hydrogen is fed to the reactor. An Agema infra-red  
20 sensitive camera 14 is used to observe the alumina support through infra-red-transparent sapphire windows via a polished metal mirror. The camera is set so that the lower end of its dynamic range corresponds to a temperature of about 40 degrees C below the feed temperature and the  
25 maximum signal is associated with a temperature about 200 degrees higher. Compositions catalyzing the reaction are revealed by the localized temperature increases (decreases for endothermic reactions) around spots 12 of that composition, as shown on photograph 18.

### Example 1a.

Catalysts are alternatively identified by conducting the reaction in the presence of strong ultraviolet and/or visible light illumination, with infra-red thermography being conducted immediately after the illumination is turned off, or through the use of a short pass filter on the illumination source to eliminate contaminating infra-red radiation.

10

### Example 2.

Referring to Figure 2, a porous alumina monolith 20 (Corning) having square or circular cross-section channels extending in a regular array through its entire thickness is treated in each channel with a solutions of catalyst precursors of differing compositions, with each composition being segregated in its own channel. After drying, calcination, etc., the activated monolith is placed in contact with a flowing potentially reactive mixture at an elevated temperature, and observed in the infra-red using an Agema model camera. The enthalpy of reaction produces localized temperature differences in the vicinity of composition exhibiting catalytic activity and these are observed as temperature variations near the exits of the channels.

25

### Example 3.

Referring to Figure 3, a porous ceramic monolith 20 of the type described in Example 2, bearing various catalyst compositions in its channels is installed in a reactor (not shown) in such a way the entire length of each channel can be observed through sapphire windows at the ends of the

30

reactor. A broad-spectrum thermal infra-red source is installed at one end of the reactor, giving an areal infra-red energy flux density. An Agema IR-sensitive camera is positioned in such a way as to observe the infra-red source directly through a significant fraction of the pores. An interferometric or other filter is installed on one side of the reactor between the camera and the infra-red source such that the light reaching the camera from the source is substantially limited to wavelengths between 4 and 4.5 microns. Observation of absorbency at this wavelength range is used to compare candidate catalyst compositions on the basis of their production of carbon dioxide, an undesired side product of the intended reaction. Catalyst compositions chosen for low carbon dioxide formation (in combination with high overall conversion activity as measured by infra-red absorbance of the desired product or by infra-red thermography) are found to have high selectivity for the desired product over the carbon dioxide side product.

#### **Example 4.**

A collection of catalyst precursor compositions is produced by automated liquid handling device, and a catalyst support particle is contacted with each composition. After further treatment to stabilize and activate the catalyst precursors, catalyst pellets are arrayed on a surface, exposed to a potentially reactive environment and their activity determined by infrared thermography.

#### **Example 5.**

Solutions of combinations of catalyst precursors are prepared in a variety of separate vessels. Each composition also contains a small quantity of a labeling material (e.g., 5 stable isotopes of the element carbon or sulfur in varying ratios). Catalyst support particles are contacted with catalyst precursor preparations, and activated. Pellets are then contacted one at a time with a potentially reactive mixture (for examples, by elutriation into an enclosed 10 volume) and their activity measured (by thermography, by spectroscopic measurement of products, or sampling of the surrounding vapor or liquid phase). Particles showing activity are collected and individually analyzed for their content of the labeling material so as to determine the 15 composition giving the desired catalytic activity.

### Example 6.

Example 2 is repeated except that only a portion of the pore length is coated with a catalyst candidate so as to allow for observation of unmodified monolith pore wall as a 20 control reference standard for optical uniformity.

### Example 7.

The emissivity of the support monolith pores of the support of Example 2 is mapped at a wavelength of interest by holding the monolith at the intended experimental 25 temperature in the absence of reactants. Digitally stored maps of the emissivity are used to normalize the infra-red energy flux measured under experimental conditions, to improve the accuracy with which local temperatures can be estimated.

**Example 8.**

A surface of high, substantially uniform emissivity is located at the end of the monolith of Example 2, away from the camera, in close radiative heat transfer/contact with the monolith channel material. The temperature of the portion of the surface closest to the open end of each channel is observed. In this case, it is necessary that gas be admitted into the channels past the uniform radiative surface, either by means of pores or by means of a small offset between the radiative surface and the monolith.

**Example 9.**

Alternatively, spots of catalysts can be deposited on the inner surface of a reactor e.g. a tube formed of the support material, and temperature of the corresponding spots on the outside of the reactor can be measured to determine by conduction whether the respective catalyst has increased or decreased in temperature under the reaction.

**Example 10.**

The process of Example 1 is repeated except that the reactants are in the liquid phase and a liquid phase assay is used to detect the activity of individual catalyst candidates.

**Example 11.**

The experiment of Example 4 is repeated except that the metal loading is directly measured by dissolving the pellet and directly analyzing the metal loading.

**Example 12.**

A sheet of alpha alumina is wash coated with particles



of porous gamma-alumina by standard methods. Solutions of oxalate salts of 12 different transition metal elements are prepared in the wells of a 24 well micro titer dish made of polystyrene. A Beckman Biomek 2000 automated liquid handling system is used to prepare dilutions and mixtures of the original stocks, again in the wells of microtiter style plates. The Biomek robot is used to deposit 40 microliter aliquots of each of the resulting solutions at defined positions on the surface of the alumina support, which is then dried, calcined and inserted into a reactor controlled at a temperature of 200 degrees centigrade. A gaseous mixture of hydrogen (97.5%) and oxygen (2.5%) is fed at a temperature of 200 degrees centigrade. An infra-red sensitive camera is used to observe the alumina support through infra-red-transparent sapphire windows. The camera is set so that its lower range corresponds to the feed temperature and the maximum signal is associated with a temperature degrees 20 degrees higher. Compositions catalyzing the reaction are revealed by the localized temperature increases around spots of that composition.

### Example 13.

A porous alumina monolith having square pores extending in a regular array through its entire thickness at a density of 25 per square inch is washcoated with alumina particles. The channels are then partially filled with solutions of differing compositions, each containing one or more metal oxalate or nitrate salts, with each composition being segregated in its own channel or set of channels. After drying and activation in the presence of hydrogen gas, the

activated monolith is placed into a sapphire-window-equipped reactor in which it can be observed in the infrared using an IR-sensitive camera. The camera is positioned in such a way as to observe the walls of the support. The relative emissivity of the support at each pixel is determined by imaging the monolith in the IR while holding the reactor and monolith at each of several constant temperatures while flowing nitrogen gas through the reactor.

10       The reactor is then fed with a gas mixture of 2.5 mole % oxygen in hydrogen. The reactor and feed temperatures are originally set to 40 degrees centigrade, and are gradually increased while the catalyst-bearing monolith is repeatedly imaged in the IR. The temperature in each cell may be judged by observing the cell at a position adjacent to the end of the catalyst-precursor-coated section of the channel, or by normalizing the observed IR energy emission by the emissivity calculated from the images taken under nonreactive conditions. The compositions in the cells showing the earliest temperature increase above the reactor temperature are useful as hydrogen oxidation catalysts.

#### Example 14.

A porous alumina monolith having square channels in a regular array extending through its entire 10 centimeter thickness at a density of 25 per square inch is washcoated with alumina particles. The channels are then partially filled with solutions of differing compositions, each containing one or more metal salts and in some cases also candidate modifiers such as barium, cesium or potassium compounds, each composition being segregated in its own

channel or set of channels.

After drying and reduction in the presence of hydrogen gas, the activated monolith is placed into a reactor in which it can be observed through a sapphire window using an IR-sensitive camera. This first window is positioned 0.5 centimeter from the surface of the monolith. The camera is positioned in such a way as to look through the window, through the channels of the support and through a second sapphire window toward a source of IR radiation.

The reactor is then fed with methane gas, mixed with oxygen and argon, in such a way that the gas flows through the channels of the monolith toward the camera. An optical filter which selectively passes IR radiation at 4.3 microns, a wavelength which is strongly absorbed by carbon dioxide, is inserted between the IR source and the camera. The effective concentration of carbon dioxide in each channel is inferred from the IR intensity at 4.3 microns seen in that channel. The reading at 4.3 microns for each pixel is divided by the reading taken through a filter selective for an IR wavelength which is near 4.3 microns, but which is not absorbed strongly by carbon dioxide, methane or water, to compensate for potential optical artifacts.

Compositions giving high concentrations of carbon dioxide after long exposures to operating conditions are useful in catalytic oxidation of methane.

### Example 15.

Solutions of combinations of catalyst precursors are prepared in a variety of separate vessels. Each composition also contains a small quantity of a labeling material (e.g.,

stable isotopes of the element sulfur in varying ratios unique to each composition). Catalyst support particles are contacted with the preparations of catalyst precursors compositions, and activated. Pellets are then contacted one at a time with a potentially reactive mixture (for examples, by elutriation into an enclosed volume) and their activity measured (by thermography, by spectroscopic measurement of products, or sampling of the surrounding vapor or liquid phase). Particles showing activity are collected and individually analyzed for their content of the labeling material so as to determine the composition giving the desired catalytic activity.

### Example 16.

15 A Teflon block having square channels in a regular array extending through its entire thickness at a density of 9 per square inch is prepared in such a way that a shallow well exists at the bottom of each channel. Each well is charged with a different polymer preparation bearing  
20 sulfonic acid groups on its surface, and a porous retaining mesh installed to keep the polymer samples in place.

The catalyst-charged monolith is placed into a reactor in which it can be observed through a window positioned 0.5 centimeter from the surface of the block. A  
25 camera is positioned in such a way as to look via through the sapphire window, through the channels of the support and through a second window, toward a source of polarized light. A polarizer is installed between the block and the camera.

A sucrose solution is fed to the reactor in such a  
30 way as to flow through the channels of the block. The angle

of rotation of polarized light in passing through the liquid in each channel is measured by rotating the polarizer to various angles, and observing the variation in brightness of the light passing through each channel. The candidate catalysts found in channels giving the greatest change in the angle of rotation are useful as catalysts of sucrose hydrolysis.

### Example 17.

Catalysts for photooxidation of hexane are identified by conducting the reaction in the apparatus of Example 16 in the presence of strong ultraviolet and/or visible light illumination, with infra-red thermography being conducted immediately after the illumination is turned off, or through the use of a short pass filter on the illumination source to eliminate contaminating infrared radiation.

### Example 18.

Samples of cyanogen bromide-activated cross linked agarose beads are exposed to solutions of alcohol oxidase at varied pH's, salt concentrations, and enzyme concentrations. After coupling of the enzyme, residual active groups are quenched with ethanolamine, the beads are washed, and each sample placed in a separate well of a multiwell plate. The plate is exposed to a flowing air stream containing ethanol vapor and observed with an Amber infrared-sensitive camera. The samples showing the greatest temperature increase are selected as highly active immobilized alcohol oxidase catalysts.

### Example 19.

Samples of cyanogen bromide activated cross linked

agarose beads are exposed to solutions of anti-alcohol oxidase antibodies at varied pH's, salt concentrations, and antibody concentrations.

- 5 After coupling of the enzyme, residual active groups are quenched with ethanolamine. The beads are washed, exposed to a solution of alcohol oxidase, washed again, and each sample placed in a separate well of a multiwell plate. The plate is exposed to a flowing air stream containing ethanol vapor
- 10 and observed with an Amber infrared-sensitive camera. The samples showing the greatest temperature increase are selected as highly active immobilized alcohol oxidase catalysts.

### Example 20.

- 15 A ceramic monolith having channels arranged in perpendicular row/column format passing through its entire thickness is washcoated with porous alumina particles and all the channels in each column are treated with the same catalyst precursors, which are activated. A potentially
- 20 reactive stream is flowed through the channels of the monolith, and a multiwavelength beam of radiation is passed over the surface of the monolith, parallel to each column, to a detector situated at the end of the column. The composition of the stream leaving the pores in that column
- 25 is estimated by processing the detector output, including Fourier transformation and/or weighted summation/differencing of the intensities at different wavelengths.

### Example 21.

- 30 Pellets bearing catalytically-active groups capable of

catalyzing the conversion of both the D-and L-stereoisomers of a reactant are treated with a variety of substances potentially capable of preferentially suppressing  
5 (temporarily or permanently) the conversion of the L-stereoisomer of that compound by that catalyst. The pellets are distributed among the wells of a multiwellplate and exposed to a mixture of the isomers of the compound to be modified. Pellets treated with the suppressor giving the  
10 greatest reduction in the activity for conversion of the L-isomer are useful in stereoselective modification of the D-isomer.

### Example 22.

A ceramic monolith having channels arranged in  
15 perpendicular row/column format passing through its entire thickness is washcoated with porous alumina particles and the channels treated with catalyst precursors, which are activated. A potentially reactive stream is flowed through the channels of the monolith. A manifold consisting of an  
20 array of tubes, each smaller than the dimensions of an individual channel, is used to introduce a stream containing ozone into the stream flowing through each channel, near its outlet. Reaction of the introduced ozone with the desired product liberates light, which is detected by a camera  
25 directed at the monolith. The catalyst composition giving the strongest light output is a useful catalyst for conversion of the reactants to the ozone-reactive desired product.

### Example 23.

30 A ceramic monolith having channels arranged in

perpendicular row/column format passing through its entire thickness is washcoated with porous alumina particles and the channels treated with catalyst precursors, which are  
5 activated and then exposed to a potential-deactivating substance. A potentially-reactive stream isflowed through the channels of the monolith. A manifold consisting of an array of tubes, each smaller than the dimensions of an individual channel, is used to sample the stream flowing  
10 within each channel. Samples from each channel in turn are introduced into a gas chromatograph-mass spectrometer combination through an arrangement of switching valves, and catalyst compositions giving the highest yield of desired products are useful in conversion of that reactive stream.

15

## Modifications

Specific compositions, methods, or embodiments discussed are intended to be only illustrative of the invention disclosed by this specification. Variations on these compositions, methods, or embodiments are readily  
20 apparent to a person of skill in the art based upon the teachings of this specification and are therefore intended to be included as part of the inventions disclosed herein. For example, statistically-designed experiments, and automated, iterative experimental process methods can be  
25 employed to obtain further reductions in time for testing. Attachment/arraying of preformed catalytic elements (especially precipitates, also single molecules and complexes such as metallocenes) onto a support, preferably by precipitating or deposition is useful in many cases.

30

Detection can involve addition of some reagent to the



stream leaving each candidate, the reagent allowing detection of a catalyst product through staining or reaction to give a detectable product, light, etc.

- 5       The supports can comprise arrays with special arrangements for uniform flow distribution, e.g., a header of multiple delivery tubes inserted into each channel in a block.

      The detection means can comprise electrochemical means,  
10 or a gamma camera for metals accumulation measurement, imaging elemental analysis by neutron activation and imaging by film or storage plate of emitted radioactivity, temperature measurement by acoustic pyrometry, bolometry, electrochemical detection, conductivity detection, liquid  
15 phase assay, preferably dissolving the support pellet and directly analyzing the metal loading; measuring refractive index in the liquid phase; observing the IR emissions of product gases directly, without the usual source and using instead the radiation hot gases emit at characteristic  
20 wavelengths.

      Other modifications can include testing for selectivity after deliberately poisoning some sites, especially in chiral catalysis, etc.

      The formulations can be supported in the form of spots  
25 or layers on the surface of a support containing wells or channels or channels extending across the entire extent of the support. The support can comprise a form of carbon, zeolite and/or plastic. The plastic can comprise a reactant. The support can hold a form of catalyst made by  
30 coprecipitation, or aluminum, or particles.

      At least one of the formulations can preferably

comprise a material selected from the group consisting of transition metals, platinum, iron, rhodium, manganese, metallocenes, zinc, copper, potassium chloride, calcium, 5 zinc, molybdenum, silver, tungsten, cobalt and mixtures of the foregoing.

The label can comprise different isotopes or different mixtures of isotopes. The reaction conditions can comprise a pressure greater than one bar absolute pressure and the 10 contact can be at a temperature greater than 100 degrees centigrade.

The method can comprise detection of temperature changes in the vicinity of a respective formulation due to reaction endotherm or exotherm. The method can comprise 15 treatment with a reducing agent. The contacting step can be carried out in the presence of compounds which modify the distribution of the metal within the porous support. The candidate catalyst formulations can be contacted in the form of spots or layers on the surface of a support containing a 20 washcoat supported by an underlayer.

The stabilizing step can be carried out with a temperature gradient or other means whereby certain candidate catalyst formulations are exposed to different temperatures. The stabilizing can comprise calcining, 25 steaming, drying, reaction, ion exchange and/or precipitation. The detection of temperature changes due to reaction can employ a correction for emissivity variations associated with differences in chemical composition.

The array of formulations to be tested can comprise 30 preformed metallocenes or other catalytic complexes fixed to a support.

The infrared radiation can be detected through the use of nondispersive infrared spectroscopy, or infrared-sensitive photographic film. The detector means can  
5 comprise means for physically scanning over an array of candidate formulations.

Observations at multiple wavelengths can be processed by mathematical manipulation e.g. transformation, weighted summation and/or subtraction, etc. Reaction activity,  
10 reactants, or products can be detected through the use of an added reaction which signals the presence of reaction or particular compounds or classes of compounds.

Chemiluminescence can be used as an indicator of reaction activity, or particular compounds or classes of compounds. A  
15 substantially collimated radiation source can be employed in product detection/imaging. Multi-tube sampling can be used to lead into a mass spectrometer, chromatograph, or optical monitor. To simulate aging, etc., the formulations can be exposed to a deleterious agent which reduces the activity of  
20 at least one formulation by at least 10%, and then optionally exposed to steam, heat, H<sub>2</sub>, air, liquid water or other different substance(s) or condition(s) which increase the activity of at least one member of the collection by at least 10% over its previously-reduced activity whereby  
25 regenerability, reactivatability, decoking, or other catalyst property is measured. The deleterious agent can comprise elevated temperature, V, Pb, Ni, As, Sb, Sn, Hg, Fe, S or other metals, H<sub>2</sub>S, chlorine, oxygen, Cl, and/or carbon monoxide.

30 Reference to documents made in the specification is intended to result in such patents or literature being

expressly incorporated herein by reference.

What is claimed is:

**CLAIMS**

1. A method of simultaneously testing or selecting catalyst formulations capable of catalyzing conversion of a given reactant or mixture of reactants, from among a collection of at least two candidate formulations, comprising in combination:

a) supporting said formulations separately on one or more supports;

b) stabilizing as necessary to fix said formulations to the support;

c) contacting the supported formulations with the reactant or reactants under reaction conditions;

d) observing the heat liberated or absorbed by the respective formulations during the course of the reaction and/or analyzing the products or reactants in the vicinity of the respective supported formulations.

2. The method of Claim 1 comprising taking a sample or observation in close proximity to the respective supported formulation, and analyzing the sample for product or reactant composition.

3. The method of Claim 1 in which the formulations are contacted while in the form of an array of spots or layers on the surface of a support.

4. A process according to Claim 1 comprising employing a support comprising silicon, chromium, zirconium and/or carbon.

5. The method of Claim 1 in which the respective formulations can be indentified by their position in an arrangement of different catalyst formulations on the support and/or by analysis of a unique label physically associated with each formulation.

6. The method of Claim 1 further comprising measuring stability by exposing the catalyst formulations to substance(s) or condition(s) which reduce the activity of at least one formulation by at least 10% and thereafter measuring activity.

7. Apparatus comprising an array of catalyst formulations comprising support means, a plurality of different formulations individually fixed to said support means and adapted to contact said formulations with a reactant or reactants under reaction conditions further comprising detector means adapted to detect relative temperature or heat absorption or emission of individual formulations in the array under the reaction conditions.

8. An apparatus according to Claim 7 wherein said detector means comprises infrared radiation-sensitive camera means, scanning diode, Raman, FTIR, NMR, ESR, GC, mass spectroscopy, GC/MS, liquid chromatography, an enzyme, a cell, an antibody, light emission spectroscopy, an additional reagent for detecting or identifying reaction or product, an infrared radiation-sensitive element, thermoelectric element, Stirling cooling apparatus and/or other spectrographic or thermographic means.

9. A catalyst comprising a formulation selected by the method of Claim 1.

10. The method of Claim 1 comprising contacting of a porous support with a solution of a salt of a metal.

11. Apparatus according to Claim 8 wherein said detector means comprises means for indentifying a candidate in an array by assigning its respective portion of an electronic image.

12. Apparatus according to Claim 8 wherein said detector means comprises electrochemical means, or a gamma camera for metals accumulation measurement, imaging elemental analysis by neutron activation and imaging by film or storage plate of emitted radioactivity, temperature measurement by acoustic pyrometry, bolometry, electrochemical detection, conductivity detection, liquid phase assay, preferably dissolving the support pellet and directly analyzing the metal loading; measuring refractive index in the liquid phase; and/or observing the IR emissions of product gases directly, without the usual source and using instead the radiation hot gases emit at characteristic wavelengths.

13. Apparatus according to Claim 8 wherein said detector means comprises means for measuring chemiluminescence as an indicator of reaction activity, or particular compounds or classes of compounds, collimated radiation source, multi tube sampling. mass spectrometer, chromatograph, or optical monitor; addition of some reagent to the stream leaving each candidate, the reagent allowing detection of a catalyst product through staining or reaction to give a detectable product, light, etc. and/or the supports comprise arrays with special arrangements for uniform flow distribution, e.g., a

header of multiple delivery tubes inserted into each channel in a block.

14. A method according to Claim 1 comprising stabilizing said formulation with a temperature gradient or other means whereby certain candidate catalyst formulations are exposed to different temperatures, calcining, steaming, drying, reaction, ion exchange and/or precipitation.

15. A method according to Claim 1 comprising simulating aging, etc., by exposing the formulations to a deleterious agent which reduces the activity of at least one formulation by at least 10%, such as elevated temperature, V, Pb, Ni, As, Sb, Sn, Hg, Fe, S or other metals, H<sub>2</sub>S, chlorine, oxygen, Cl, and/or carbon monoxide; and then exposing to steam, heat, H<sub>2</sub>, air, liquid water or other different substance(s) or condition(s) which increases the activity of at least one of the formulations by at least 10% over its previously-reduced activity whereby regenerability, reactivatability, decoking, or other catalyst property is measured.

16. The method of Claim 1 comprising the detection of temperature changes due to reaction comprising a correction for emissivity variations associated with differences in chemical composition.

17. A method of Claim one wherein said formulations comprise a material selected from the group consisting of transition metals, platinum, iron, rhodium, manganese, metallocenes, zinc, copper, potassium chloride, calcium, zinc, molybdenum, silver, tungsten, cobalt and mixtures of the foregoing



18. A method of Claim 1 comprising detection of temperature changes in the vicinity of a respective formulation due to reaction endotherm or exotherm. The method can comprise treatment with a reducing agent. The contacting step can be carried out in the presence of compounds which modify the distribution of the metal within the porous support. The candidate catalyst formulations can be contacted in the form of spots or layers on the surface of a support containing a washcoat supported by an underlayer.

19. A method of Claim 1 comprising processing observations at multiple wavelengths by mathematical manipulation e.g. transformation, weighted summation and/or subtraction, etc. ; detecting reaction activity, reactants, or products through the use of an added reaction which signals the presence of reaction or particular compounds or classes of compounds and/or using chemiluminescence as an indicator of reaction activity.

20. Each invention described herein.

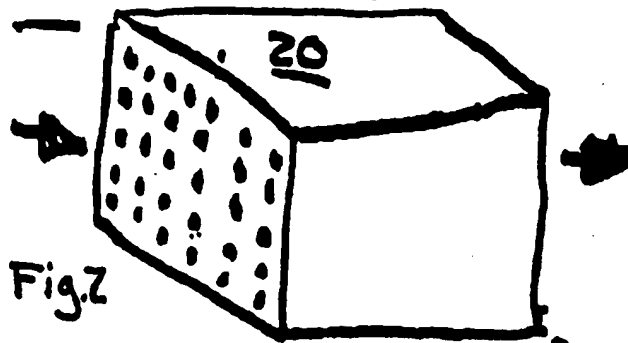


Fig. 2

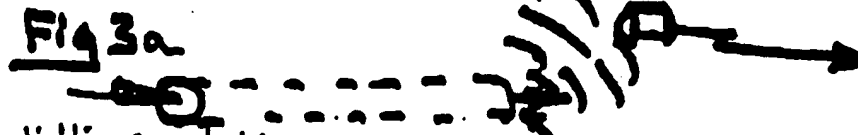
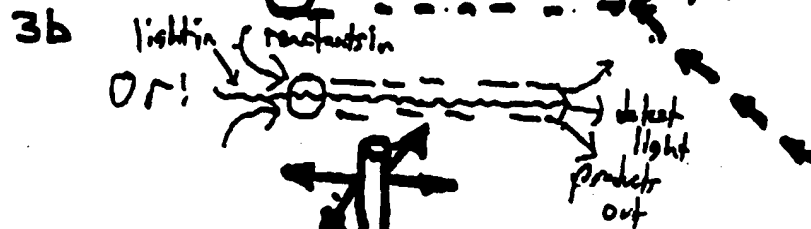


Fig. 3a



3b

Fig. 4

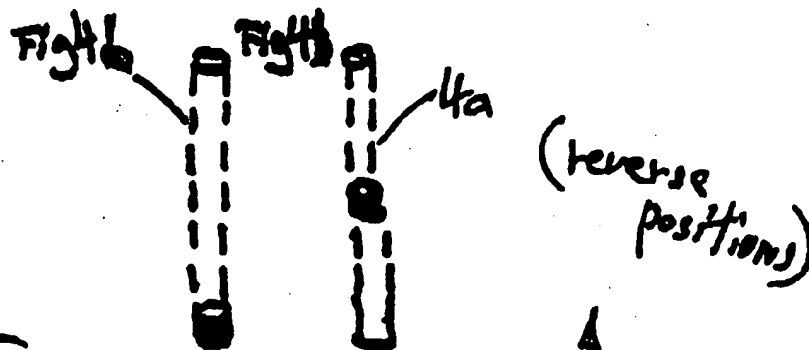
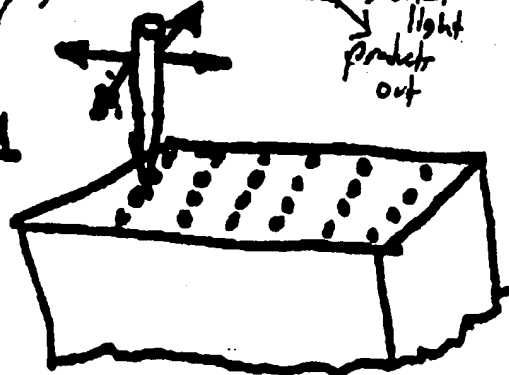


Fig. 5

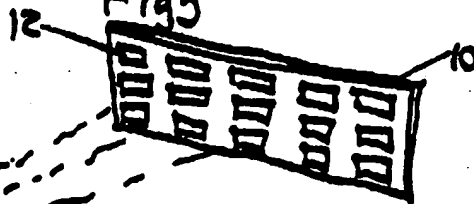


Fig. 6a

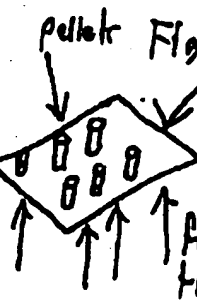


Fig. 6b

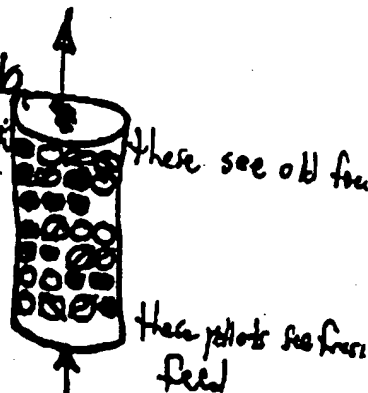


Fig. 6c

# INTERNATIONAL SEARCH REPORT

In ational application No.   
 PCT/US97/02756

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01N 31/10  
US CL :436/37, 147, 159, 161, 164, 173, 173; 422/62, 93, 104, 196, 197  
According to International Patent Classification (IPC) r to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/37, 147, 159, 161, 164, 173, 173; 422/62, 93, 104, 196, 197

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*    | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.                                  |
|--------------|---|--|
| X,P          | F. C. Moates et al. "Infrared Thermographic Screening of Combinatorial Libraries of Heterogeneous Catalysts" Industrial and Engineering Chemistry Research, December 1996, Vol. 35, No. 12, pages 4801 - 4803, see entire document. | 1-20   |
| X<br>--<br>Y | B. Posner et al. "Catalytic Antibodies: Perusing Combinatorial Libraries" Trends in Biochemical Science, April 1994, Vol. 19, pages 145-150, see entire docuement.  | 1 - 5 , 7 -<br>9,12,13,19-20<br>-----<br>6,10-11,14-18 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

|   |     |  |
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Date of the actual completion of the international search

09 JUNE 1997

Date of mailing of the international search report

08 JUL 1997

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/02756

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|-----------|---|-----------------------|
| Y         | C. E. Berkoff et al. "A Multiple Cell Apparatus for the Rapid Evaluation of Catalyzed Chemical Reactions" Chemistry and Industry, January 1981, No. 2, pages 68 - 69, see entire document.          | 1-20                  |
| Y         | US, 3,431,077 A (DANFORTH) 04 March 1969, see entire document.  | 1-20                  |
| Y         | US 4,099,923 A (MILBERGER) 11 July 1978, see entire document.   | 1-20                  |
| Y         | J. T. Richardson et al. "Characterization and Deactivation of NiO-ThO <sub>2</sub> Catalysts" Applied Catalysis, 1989, Vol. 48, pages 159 - 176, see entire document.                               | 6-9,12-20             |
| A         | V. R. Choudhary et al. "Isomerization of n-Butene to Isobutene I. Selection of Catalyst by Group Screening" Journal of Catalysis, 1971, Vol. 23, pages 54 - 60.                                     | 1-20                  |
| A         | M. P. Harold et al. "An Experimental Study of Steady-State Multiplicity Features of Two Parallel Catalytic Reactions" Chemical Engineering Science, 1985, Vol. 40, No. 1, pages 39 - 52.            | 1-20                  |
| A         | D. Kreuzer et al. "Kinetic Characterization of Alumina-Supported Nickel Catalysts for the Methanation of Carbon Monoxide" Applied Catalysis, 1985, Vol. 15, pages 117 - 126.                        | 1-20                  |
| A         | A. Govil et al. "Thermal Sensitivity of Multi-Tube Reactors" Hungarian Journal of Industrial Chemistry Veszprem, 1989, Vol. 17, pages 545 - 561   | 1-20                  |
| A         | F. Schuth et al. "Synchrony and the Emergence of Chaos in Oscillations on Supported Catalysts" Journal of Chemical Physics, January 1990, Vol. 92, No. 1, pages 745 - 756.                          | 1-20                  |
| A         | D. S. Tawfik et al. "catELISA: A Facile General Route to Catalytic Antibodies" Proceedings of the National Academy of Sciences, USA, January 1993, Vol. 90, pages 373 - 377.                        | 1-20                  |
| A         | K. D. Janda et al. "Direct Selection for a Catalytic Mechanism from Combinatorial Antibody Libraries" Proceedings of the National Academy of Sciences, USA, March 1994, Vol. 91, pages 2532 - 2536. | 1-20                  |

**INTERNATIONAL SEARCH REPORT****International application No.**  
**PCT/US97/02756****C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|-----------|---|-----------------------|
| A         | F. M. Menger et al. "Phosphatase Catalysis Developed via Combinatorial Organic Chemistry" Journal of Organic Chemistry, 1995, Vol. 60, pages 6666 - 6667. | 1-20                  |

# INTERNATIONAL SEARCH REPORT

International application No.   
PCT/US97/02756

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

STN search in CA and APILIT files, search terms: catal?, screening, formulat?, app, apparatus, device, multip?, dta, carbonate, validat?, test, gas phase, hydrocrack?, screen?, det##, detect?, determin?, measur?, monitor?, test?, analysis, combin?, librar?, character?, spot, dot, pellet, muki?, combinatorial, library, computer, infrared

May 24, 1999

Patent family & legal status on WO 97/32208 and WO 98/07026

(Attn: Maryann Maas)

File 348: European Patents 1978-1999/May W18

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\*File 348: \*\* NEW FEATURE \*\* English language translations of French and German abstracts now searchable. See HELP NEWS 348 for info.

Set Items Description

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S1 1 PN="WO 9732208"

TI - Simultaneous testing or selecting of catalyst formulations - by stabilising individual formulations to support(s), contacting with reactant(s) and measuring and/or analysing e.g. heat liberated

PA - (TECH-) TECHNOLOGY LICENSING CO LLC

IN - WILLSON RC

PR - 96.06.17 96US-664836 96.02.28 96US-012457

NUM - 3 patent(s) 76 country(s)

PN -- WO9732208 A1 97.09.04 \* (9741) E 35p G01N-031/10

NW: \*AL \*AM \*AT \*AU \*AZ \*BA \*BB \*BG \*BR \*BY \*CA \*CH \*CN

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NL OA PT SD SE SZ UG

- AU9719679 A 97.09.16 (9803) G01N-031/10

Based on WO9732208

- EP-883806 A1 98.12.16 (9903) E G01N-031/10

R: CH DE ES FR GB IT LI NL

Based on WO9732208

AP -- 97WO-US02756 97.02.25; - 97AU-019679 97.02.25

- 97EP-907768 97.02.25 97WO-US02756 97.02.25

AB - WO9732208 A

Simultaneously testing or selecting catalyst formulations capable of catalysing the conversion of given reactant(s) comprises: (a) supporting the formulations separately on support(s); (b) stabilising as necessary to fix the formulations to the support(s); (c) contacting the supported formulations with reactant(s) under reaction conditions; and (d) observing heat liberated or absorbed by the respective formulations during the course of the reaction and/or analysing the products or reactants in the vicinity of the formulations.

Also claimed is an apparatus comprising an array of catalyst formulations comprising supports, different formulations individually fixed to the supports and adapted to contact the formulations with reactant(s) and detectors adapted to detect relative temperature or heat absorption or emission of formulations in the array under reaction conditions.

USE - Used for testing and/or selecting catalyst formulations for conversion reactions e.g. hydrocarbon conversions, alkylation, gasoline sweetening, etc..

ADVANTAGE - The process reduces the time and labour involved in screening for improved catalysts and allows the

screening and/or testing of several catalysts simultaneously in  
a single set-up. (Dwg.0/6)

1/5/1

DIALOG(R)File 348:European Patents

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CATALYST TESTING PROCESS AND APPARATUS

VERFAHREN UND VORRICHTUNG ZUM TESTEN VON KATALYSATOREN

APPAREIL ET PROCEDE D'ESSAI DE CATALYSEURS

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LEGAL REPRESENTATIVE:

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PATENT (CC, No, Kind, Date): EP 883806 A1 981216 (Basic)

WO 9732208 970904

APPLICATION (CC, No, Date): EP 97907768 970225; WO 97US2756 970225

PRIORITY (CC, No, Date): US 12457 P 960228; US 664836 960617

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INTERNATIONAL PATENT CLASS: G01N-031/10;

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Application: 971126 A1 International application (Art. 158(1))

Application: 981216 A1 Published application (A1with Search Report  
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980731

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LANGUAGE (Publication,Procedural,Application): English; English; English

S2 1 PN="WO 9807026"

TI - Testing chemical reactions carried out in parallel in reactors  
- using miniaturised reactors and reaction mixture or reaction  
products are analysed during reaction time

PA - (FARH ) HOECHST AG; (FARH ) HOECHST RES & TECHNOLOGY DEUT GMBH & CO

IN - HOPPE H, MICULKA C, WINDHAB N

PR - 96.08.15 96DE-1032779

NUM - 3 patent(s) 21 country(s)

PN -- DE19632779 A1 98.02.19 \* (9813) 7p G01N-035/00

- WO9807026 A1 98.02.19 (9814) G 22p G01N-031/10

NW: \*AU \*CA \*JP \*US

RW: AT BE CH DE DK ES FI FR GB GR IE IT LU MC NL PT SE

- AU9743796 A 98.03.06 (9830) G01N-031/10

Based on WO9807026



AP -- 96DE-1032779 96.08.15  
- 97WO-EP04369 97.08.12  
- 97AU-043796 97.08.12  
FN - WPI2TDZ1.GIF  
AB - DE19632779 A

The test method is carried out in miniaturised reactors, and the reaction mixture or the reaction products are analysed during the reaction time. The reaction products are supplied continuously to the reactors and the products are continuously drawn from the reactors.

The reactions are carried out at different temperatures, preferably with temperatures in a range from room temperature up to and including 600 degrees C or at differing pressures, preferably with absolute pressures of from 10 power(-3) to 10 power(3) bar, especially preferably from 10 power(-2) to 200 bar.

ADVANTAGE - Multiple of reactions under practically identical conditions and with comparatively small substance and sample amounts can be carried out quickly, cost effectively and reproducibly and simultaneously spectroscopically tested. (Dwg.1/2)

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DIALOG(R) File 348:European Patents

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PATENT (CC, No, Kind, Date):

WO 9807026 980219

APPLICATION (CC, No, Date): WO 97EP4369

INTERNATIONAL PATENT CLASS: G01N-031/10

CITED PATENTS (WO A): US 4099923 A; US 3431077 A; US 5266270 A

LEGAL STATUS (Type, Pub Date, Kind, Text):

Application: 980624 A1 International application (Art. 158(1))

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